

## The Reaction of *cis*-9-Octadecene and Related Compounds with Aqueous Perchloric Acid<sup>1</sup>

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The heterogeneous reaction of *cis*-9-octadecene with aqueous 67% deuterioperchloric acid has been studied with respect to the reaction variables involved, *i.e.*, reaction time, stirring rate, temperature, molar ratio of reactants, and strength of inorganic acid. High yields of isomeric octadecenes were obtained. The rate of double-bond migration was significantly faster than the rate at which deuterium was incorporated into the product. Small amounts of octadecyl perchlorates are formed in the reactions. *cis*-9-Octadecene and 1-octadecene were allowed to react with aqueous deuterioperchloric acid in the presence of stearic acid; migration of the double bond occurs by means of a reversible acid-olefin esterification reaction. The octadecene product shows a more extensive isomerization than is obtained in the absence of stearic acid; it is also comparatively heavily deuterated. Reactions of 1- and 9-octadecanol, both in the presence and absence of stearic acid, emphasize the differences in behavior between primary and secondary compounds.

Past studies<sup>4</sup> in this laboratory have been concerned with the optimum conditions for the preparation of  $\gamma$ -stearolacetone from the reaction of aqueous 70% perchloric acid with various C<sub>18</sub> monounsaturated and monohydroxy fatty acids and with an investigation of the types and amounts of reaction by-products. This has led us to an examination of the reaction of 9- and 1-octadecenes and -octadecanols with aqueous deu-

terioperchloric acid and the changes brought about in the system by the introduction of stearic acid. The addition of stearic acid to the reaction mixture has meant that, as in the past studies,<sup>4</sup> the functional groups, olefin (or hydroxyl) and carboxylic acid, are present, albeit in two molecules rather than in a single molecule.

**The Reaction of *cis*-9-Octadecene with Aqueous Deuterioperchloric Acid.**—A series of reactions of *cis*-9-octadecene with aqueous 67% deuterioperchloric acid was carried out changing one at a time the reaction variables of time, stirring rate, temperature, molar ratio of deuterioperchloric acid to *cis*-9-octadecene used, and strength of inorganic acid. The amount of *cis*-9-octadecene used and the size of the reaction vessel and magnetic stirring bar were kept fixed for all reactions.

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(3) Agricultural Research Service, U. S. Department of Agriculture.

(4) J. S. Showell, W. R. Noble, and D. Swern, *J. Org. Chem.*, **33**, 2697 (1968).

TABLE I  
EFFECT OF REACTION TIME ON ISOMER DISTRIBUTION  
OF OCTADECENE PRODUCT<sup>a</sup>

	Mole %			
	$\frac{1}{6}$ hr	$\frac{1}{2}$ hr	$\frac{3}{4}$ hr	3 hr
$\Delta^{1,2}$				<sup>b</sup>
$\Delta^{2,3}$				0.9
$\Delta^{3,4}$				2.5
$\Delta^{4,5}$				3.8
$\Delta^{5,6}$				7.0
$\Delta^{6,7}$		1.8	4.2	15.3
$\Delta^{7,8}$	2.4	6.6	10.4	20.6
$\Delta^{8,9}$	10.3	31.4	35.8	24.8
$\Delta^{9,10}$	87.3	60.2	49.6	25.1
	%			
Recovery of octadecene	97	98	96	97
Yield of octadecyl perchlorate	0.4	1.4	1.8	2.6

<sup>a</sup> 100° reaction; medium stirring rate; 1.0:1.0 molar ratio of *cis*-9-octadecene to deuterioperchloric acid. <sup>b</sup> No terminal olefin was detected.

**Effect of Reaction Time.**—A series of separate reactions (Table I) at 100°, in which a constant ("medium," see Experimental Section) stirring rate and a 1.0:1.0 molar ratio of deuterioperchloric acid to *cis*-9-octadecene were used, showed that as the reaction times were increased from  $\frac{1}{6}$  hr through to 3 hr there is a corresponding increase in the extent to which the octadecene has been isomerized.

**Effect of Stirring Rate.**—A 3-hr, 100° reaction, in which a 1.0:1.0 molar ratio of reactants that remained unstirred was used, yielded an octadecene product in which 54% of the double bond was in the  $\Delta^{9,10}$  position and no isomerization beyond  $\Delta^{6,7}$  had occurred. Reactions at 100° for 1, 2, and 6 hr, with a fast stirring rate, gave very similar octadecene isomer distributions, comparable with that obtained in 3 hr with the medium stirring rate (Table I).

The dependence on reaction time and rate of stirring is to be expected for a heterogeneous reaction.

**Effect of Temperature.**—The octadecene isomer distributions obtained from reactions at 85, 100, and 115° (3 hr, 1.0:1.0 molar ratio of reactants, medium stirring rate) were very similar but with some increase in shift of double bond away from the center of the molecule with increase in temperature. The respective yields for the  $\Delta^{9,10}$  isomer were 28, 25, and 23%; isomerization extended to  $\Delta^{4,5}$ ,  $\Delta^{3,4}$ , and  $\Delta^{2,3}$ .

**Effect of Molar Ratio of Reactants.**—The use of lesser amounts of aqueous deuterioperchloric acid resulted in a more restricted octadecene isomerization for 3-hr reactions at 100° with the medium stirring rate. For a 0.02:1.00 molar ratio of deuterioperchloric acid to *cis*-9-octadecene the product contained 76%  $\Delta^{9,10}$  isomer and decreasing amounts of  $\Delta^{8,9}$ ,  $\Delta^{7,8}$ , and  $\Delta^{6,7}$ . A ratio of 0.11:1.00 gave 50%  $\Delta^{9,10}$  with isomerization extending to  $\Delta^{5,6}$ .

The decrease in octadecene isomerization with decrease in amount of inorganic acid was expected in the light of past studies<sup>4</sup> on oleic acid-perchloric acid reactions. There it appears that the principal reaction occurs in the perchloric acid phase and the reaction at the interface does not make any significant contribution. However, the above results could equally well be explained on the basis that, for a heterogeneous reaction and a given stirring rate, the increase in surface area

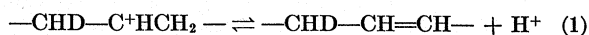
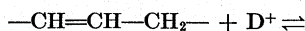
between phases (from an increase in amount of inorganic acid) will result in increase in octadecene isomerization. This would apply whether the reaction was occurring in one or both phases, or at the interface.

**Effect of Perchloric Acid Strength.**—The aqueous deuterioperchloric acid used throughout this work contained 67% by weight of deuterioperchloric acid in the aqueous solution, *i.e.*, 28.5 mole % in DClO<sub>4</sub>. The 3-hr, 100° reaction of *cis*-9-octadecene with this aqueous deuterioperchloric acid may be usefully compared with that of an aqueous perchloric acid, 66% by weight, 26.0 mole % of HClO<sub>4</sub>. More isomerization was produced by the deuterio acid (25%  $\Delta^{9,10}$ , isomerization to  $\Delta^{2,3}$ ) than the hydrogen acid (42%  $\Delta^{9,10}$ , isomerization to  $\Delta^{4,5}$ ); a reaction with a 50:50 mixture of the two inorganic acids gave an intermediate double-bond distribution (31%  $\Delta^{9,10}$ , isomerization to  $\Delta^{3,4}$ ). It is likely that the acid strengths are at greater variance than is reflected by the 2.5% molar difference, owing to secondary isotope effects in favor of increased strength of the deuterio acid.<sup>5</sup>

**Formation of Perchlorate Ester.**—Octadecyl perchlorates were found as minor-by-products (~2%) in the *cis*-9-octadecene-aqueous deuterioperchloric acid reactions (*e.g.*, Table I), and in greater yield (14%) in a 1-octadecene reaction (Table II). The presence of even 1–2% perchlorate in the crude reaction product was readily detected by the strong and characteristic infrared (ir) absorption<sup>6</sup> at 1250 and 1220 (doublet), 1020, and 710 cm<sup>-1</sup>. The yield of octadecyl perchlorate was calculated from a chlorine analysis on the crude (DClO<sub>4</sub>-free) reaction product, as it was found that the perchlorate was not eluted from either a silicic acid or Florisil chromatographic column. A violet band that appeared on the head of the column when the eluting solvent was changed from Skellysolve B to Skellysolve B containing 1–2% diethyl ether may indicate decomposition of the perchlorate.

The perchlorate formed in reactions of a primary alcohol, 1-octadecanol (see below), provided the only example in this work where these compounds survived column chromatography.

**Reaction Mechanism of Double-Bond Migration.**—The isomerization of *cis*-9-octadecene by aqueous deuterioperchloric acid would be expected to occur by mechanism 1.



A sequence of reactions would eventually set up an equilibrium distribution of hydrogen and deuterium between the organic and inorganic material. This would result in 4.8 deuterium atoms/mol in the octadecene product for a 1.0:1.0 molar ratio reaction (1 mol of deuterioperchloric acid is associated with 2.5 mol deuterium oxide). On the basis of the above mechanism an extensively isomerized octadecene product could be heavily deuterated (up to 4.8 atoms/mol). Table III shows some typical deuteration results.

A comparison of Tables I and III shows there is a difference in double-bond migration and deuteration rates. For example, in a 3-hr reaction, a total of 65%

TABLE II  
EFFECT OF STEARIC ACID ON ISOMER DISTRIBUTION OF OCTADECENE PRODUCT<sup>a</sup>

	Mole %				
	<i>cis</i> -9-Octadecene			1-Octadecene	
	<i>x</i> , 1.0, <i>t</i> , $\frac{1}{3}$	<i>x</i> , 1.0, <i>t</i> , 1	<i>x</i> , 0.9, <i>t</i> , 3	<i>x</i> , 0, <i>t</i> , 3	<i>x</i> , 1.0, <i>t</i> , 3
$\Delta^{1,2}$				1.4 <sup>b</sup>	
$\Delta^{2,3}$	0.9	5.7	12.8	56.7	17.2
$\Delta^{3,4}$	3.2	8.5	13.3	26.5	12.9
$\Delta^{4,5}$	5.3	9.7	13.2	11.6	14.9
$\Delta^{5,6}$	7.4	12.1	12.9	3.3	13.5
$\Delta^{6,7}$	15.9	16.1	14.4	0.5	13.6
$\Delta^{7,8}$	18.7	16.1	11.8		10.5
$\Delta^{8,9}$	23.7	16.1	10.8		8.9
$\Delta^{9,10}$	24.9	15.7	10.8		8.4
	%				
Recovery of octadecene	73.8	74.4	75.2	84.6	64.3
Yield of octadecyl stearate	24.6	24.2	22.7		32.2
Recovery of stearic acid	74.6	76.1	72.4		65.3

<sup>a</sup> 100°; *t*, hours of reaction; 1.0:1.0:*x* molar ratio of octadecene to deuterioperchloric acid to stearic acid; medium stirring rate.

<sup>b</sup> 14.3% yield of octadecyl perchlorate.

TABLE III  
EFFECT OF REACTION TIME ON DEUTERIUM COMPOSITION OF OCTADECENE PRODUCT<sup>a</sup>

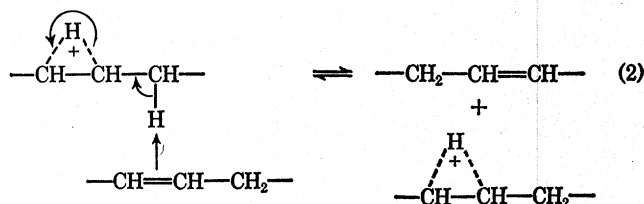
	Mole %			
	$\frac{1}{6}$ hr	$\frac{1}{2}$ hr	$\frac{3}{4}$ hr	3 hr
0 D	99.0	97.9	96.5	65.0
1 D	<1.0	1.6	30.3	30.3
2 D		0.5	0.6	4.4
3 D				0.3
Average number of deuterium atom/mol	0.01	0.02	0.04	0.40

<sup>a</sup> 100° reaction; medium stirring rate; 1.0:1.0 molar ratio of *cis*-9-octadecene to deuterioperchloric acid.

of the octadecene product contains no deuterium at all (Table III), though 75% of the unsaturation is outside the  $\Delta^{9,10}$  position (Table I). Again, in a 10-min reaction, 99%+ of the octadecene product contains no deuterium (Table III), although 13% has undergone positional isomerization (Table I). Even in the 6-hr reaction with a faster stirring rate there was only an average of 0.76 deuterium atom/mol in the product (55.4% 0 D, 35.9% 1 D, 7.9% 2 D, and 0.7% 3 D).

If we assume that the above ionic mechanism operates and that the bulk of the reaction occurs in the organic phase, then the difference in double-bond migration and deuteration rates may be a simple artifact of the primary isotope effect which would be relatively large in the nonpolar phase; this is particularly so since the initial rates of hydrogen enrichment *via* exchange is probably much greater than the rate of deuterium enrichment *via* diffusion at the interface.<sup>7</sup>

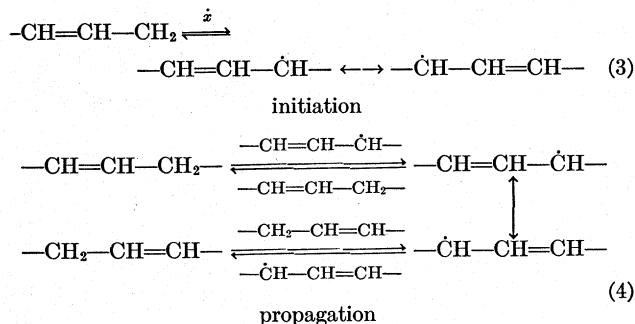
Other suggestions for ionic mechanisms can be invoked to explain the low amount of deuterium incorporation in the product but suffer from the disadvantage of having no precedent, *e.g.*, an ionic chain mechanism with a propagation step of the type shown in reaction 2.



(7) Reviewer's suggestion.

The presence of perchlorate esters in the products would be expected to accompany either ionic mechanism, and their ionization could be part of a chain-initiation process.<sup>7</sup>

Another possible explanation is that the reaction is not ionic at all but is a radical process, initiated by the presence of small amounts of oxides of chlorine (eq 3 and 4).



**Reaction of *cis*-9- and 1-Octadecene with Aqueous Deuterioperchloric Acid-Stearic Acid.**—The addition of 0.9–1.0 molar ratio of stearic acid as a third component to a *cis*-9-octadecene–aqueous deuterioperchloric acid reaction mixture produces a different system. For example a 3-hr reaction results in a more extensively isomerized octadecene product (Table II; *cf.* Table I) and also considerable greater deuterium incorporation in the product (Table IV; *cf.* Table III). The same type of differences are found between 1-octadecene–aqueous deuterioperchloric acid and 1-octadecene–aqueous deuterioperchloric acid–stearic acid reactions (Tables II and IV).

The dependence of double-bond isomerization and deuteration of octadecene product on reaction time is shown for *cis*-9-octadecene (Tables II and IV). For a 1.0 molar ratio of stearic acid the level of octadecyl stearate is 24% at  $\frac{1}{3}$  and 1 hr.

Hydrolyses with molten alkali of the octadecyl stearates from the 3 hr *cis*-9- and 1-octadecene reactions yielded all possible isomeric secondary octadecanols and stearic acid. The octadecanol hydrolysis products were heavily deuterated, comparable with the corresponding octadecene products, and the stearic acid hydrolysis products contained no incorporated deuterium (if any were present in the  $\alpha$  position it would be

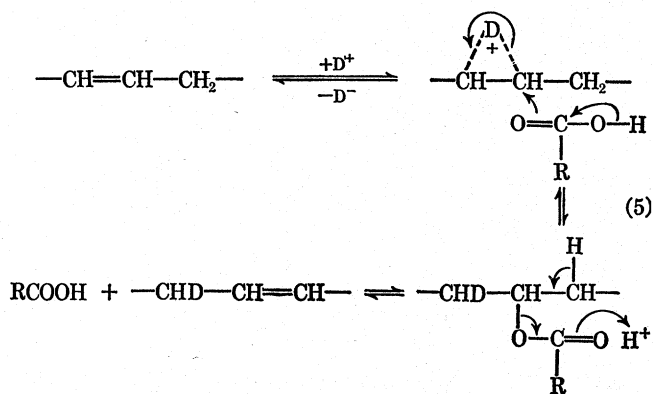
EFFECT OF STEARIC ACID ON DEUTERIUM COMPOSITION OF OCTADECENE PRODUCTS<sup>a</sup>

Average number of deuterium atoms/mol	0.57	2.06	3.32	0.25	2.48
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<sup>a</sup> 100°; *t*, hours of reaction; 1.0:1.0:*x* molar ratio of octadecene to deuterioperchloric acid to stearic acid; medium stirring rate.

exchanged out in the molten alkali). The free stearic acid recovered from both the *cis*-9- and 1-octadecene reactions contained very little deuterium (0.004 deuterium atom/mol).

These results suggest that in the octadecene–aqueous deuterioperchloric acid–stearic acid reaction system the double bond migrates along the octadecene chain by a series of reversible acid–olefin esterification reactions (eq 5).



The reversibility of the esterification reaction was shown by running 0.50 g of the octadecyl stearate product from the 1-octadecene-stearic acid-aqueous deuterioperchloric acid in another 100°, 3-hr reaction with a 1.0 molar ratio of aqueous deuterioperchloric acid; apart from recovered octadecyl stearates (26.0%), the products were stearic acid (63.9%) and octadecenes (49.4%). Although the latter had a double-bond distribution very similar to the original octadecene product, the existence of a considerable further reaction was shown by the fact that the octadecene contained an average of 5.80 deuterium atoms/mol (compared with 2.48 deuterium atoms/mol for the first run product), and the commonest deuterated species contained 5 deuterium atoms (14.05%) with a gradual tailing off to a 16 deuterated species (0.07%).

Perchloric acid has found use as a catalyst for the esterification of carboxylic acids by olefins.<sup>8,9</sup> As a rule interest has centered on a maximum yield of ester and

little attention has been paid to ester composition or the composition of the recovered olefin. However, Placek and Bickford<sup>10</sup> found that, in the perchloric acid catalyzed reaction of petroselinic acid and formic acid, the addition of the formic acid took place chiefly at the 5-, 6-, 7-, and 8-carbon positions. The authors note the formation of unsaturated compounds when 10-formoxy-octadecanoic acid was subjected to formoxylation conditions and postulate that migration of the double bond from the 6,7 position of petroselinic acid may be due to the reversible formation of formate ester. They place equal importance on the alternative suggestion that an addition-elimination sequence of the catalyst would result in migration of the double bond. By analogy with the present work it would seem likely that the former explanation is correct.

Before leaving the topic of the effect of stearic acid on the octadecene-aqueous deuterioperchloric acid reactions it should be pointed out that the presence of a 1.0 molar ratio of stearic acid results in the virtual disappearance of octadecyl perchlorates as a product. This is true even for 1-octadecene, for which the perchlorate yield in the absence of stearic acid is much higher than is obtained from a *cis*-9-octadecene reaction. In no octadecene reaction, in presence or absence of stearic acid, was more than a trace of branched-chain product detected. In studies on oleic acid,<sup>4</sup> 10% of the  $\gamma$ -stearolactone product was branched-chain material.

**Reaction of 1- and 9-Octadecanols with Aqueous Deuterioperchloric Acid.**—The reactions of primary and secondary alcohols with aqueous deuterioperchloric acid showed marked differences. 1-Octadecanol in a 3-hr, 100° reaction, with a 1.0:1.0 molar ratio of reactants and medium stirring rate, gave a heavily deuterated hydrocarbon (8%) containing some perchlorate ester, di-*n*-octadecyl ether<sup>11</sup> (20.6%), and recovered 1-octadecanol (41.6%).

The reaction repeated with the addition of a 1.0 molar ratio of stearic acid gave *n*-octadecyl stearate (94.2%), and recovered stearic acid (2.9%) and 1-octadecanol (1.0%), and also *n*-octadecyl perchlorate (1.2%). The latter material showed extremely strong perchlorate absorption in the ir spectrum. The reactions with 1-octadecanol represent the only cases where

perchlorate ester has survived the column chromatography used to separate the reaction products.

The reaction of 9-octadecanol with aqueous deuterio-perchloric acid involves a rapid dehydration of the alcohol to olefin.<sup>11</sup> After 10 min at 100° and with the medium stirring rate, the recovered product was essentially 100% olefin. A 3-hr reaction time resulted in only a small amount of isomerization, no doubt because the elimination of water from the alcohol causes a critical dilution of the inorganic acid (92% yield of olefin; 41%  $\Delta^9$ ,<sup>10</sup> no isomerization beyond  $\Delta^{5,6}$ ). Molar equivalents of 9-octadecanol, deuterio-perchloric acid, and stearic acid in a 20-min reaction gave 55% olefin (49%  $\Delta^9$ ,<sup>10</sup> no isomerization beyond  $\Delta^{5,6}$ ), octadecyl stearates (27%), and recovered stearic acid (67%).

### Experimental Section<sup>12a</sup>

**Materials. Aqueous Deuterio-perchloric Acid.**—All glassware was soaked overnight in nitric acid and washed with distilled water before use. Heavy water (99.8 atom %, 25 g) was added to Eastman Kodak aqueous 72% perchloric acid<sup>12b</sup> (100 ml) in a 500-ml round-bottomed flask fitted with a distillation head, condenser, and receiving flask. A slight positive pressure of nitrogen was applied and the flask contents were stirred with a magnetic bar. The flask was slowly heated by means of a Wood's metal bath and water was distilled off (over 1 hr) in the bath-temperature range 100–190°. The bath temperature was allowed to fall to 90° before the addition of more heavy water (25 g). Water was again distilled off by a slow rise in bath temperature to 190°, followed by a cooling to 90°. The procedure was repeated to give a total of eight separate additions of heavy water (25 g each) and eight removals of water (average of 22.5 ml each). The aqueous acid ( $d^{25}$  1.7322) was calculated to be 90% deuterium enriched and contained 67.3% by weight deuterio-perchloric acid in the heavy water solution.

**cis-9-Octadecene.**—The preparation was conducted by J. R. Russell of these laboratories by the lithium aluminum hydride reduction of oleyl tosylate. A solution of oleyl alcohol (676 g, 2.74 mol) in pyridine (680 g) was added slowly (1 hr) to a stirred (Vibro-mixer) solution of *p*-toluenesulphonyl chloride (604 g, 3.17 mol), at 20°. The stirring was continued a further 4 hr before addition of ice-water (volume twice that of reactants) and benzene (2 l.), followed by a few minutes further stirring. Salt was added to break the emulsion and the organic layer was washed several times with a saturated salt solution. Concentrated hydrochloric acid (1 l.) was chilled to -10° and added slowly to the stirred product. The organic layer was then washed several times with salt water and water, respectively, and then dried ( $\text{Na}_2\text{SO}_4$ ) before removal of the solvent on a rotary evaporator to give the crude reaction product (890.9 g). Molecular distillation gave oleyl tosylate (829.9 g, 72%), bp 170° (3 min),  $n_D^{25}$  1.4913.

**Anal.** Calcd for  $\text{C}_{25}\text{H}_{45}\text{O}_2\text{S}$ : C, 71.04; H, 10.02; S, 7.59. Found: C, 71.20; H, 10.15; S, 7.60.

Oleyl tosylate (627.4 g) was added dropwise to tetrahydrofuran (2 l.) containing lithium aluminum hydride (64.5 g, 1.48 mol) and the mixture was stirred and brought to reflux (positive nitrogen pressure). Sodium hydroxide (ca. 5 g) was added. Overnight reflux produced gellike material; benzene (2 l.) was added; and the mixture was poured into an equal volume of water. After repeated benzene extractions, the extract was washed several times with an aqueous sodium hydroxide solution. The extract was concentrated to recover an amber liquid (210 g) which was chromatographed on a silicic acid column. The product (206 g) from the elution was distilled on a spinning-band column to give *cis*-9-octadecene (195 g, 53%), bp 95–98° (0.5 mm),  $n_D^{25}$  1.4442. The ir spectrum showed no detectable *trans* isomer (lack of 968- $\text{cm}^{-1}$  band in liquid film) and oxidative cleavage showed the absence of any positional isomers.

**1-Octadecene.**—Commercial 1-octadecene was chromatographed on a Florisil column. Gas-liquid partition chromatography (glpc) (SE-30, 200) showed a single peak; oxidative cleavage showed >95% of the double bond in the terminal position.

**9-Octadecanol.**—Material was available from a previous preparation<sup>13</sup> involving the lithium hydride reduction of *cis*-9,10-epoxyoctadecanol. Recrystallization of the reaction product gave 9-octadecanol, mp 58.5°.

**1-Octadecanol.**—Commercial 1-octadecanol was purified in these laboratories (M. V. Nunez) by redistillation, followed by several recrystallizations from acetone (0°) of the fraction with bp 128.5–136.0° (0.05 mm). The 1-octadecanol [mp 58.3°,  $n_D^{20}$  1.4382, % hydroxyl 6.21 (theoretical 6.29)] was estimated by glpc to be 98.5% pure.

**Stearic Acid.**—Purified in these laboratories by several recrystallizations from triethylamine-methanol. The stearic acid obtained had mp 69.3–69.5° and was estimated by glpc to be 99.7% pure.

**Aqueous Deuterio-perchloric Acid Reactions.**—All reactions were carried out in the same reaction vessel, a jacketed vessel of internal diameter 2.8 cm and rounded at the bottom with a well 1.0 cm deep, using the same magnetic stirring bar (1.3 cm long, 0.3 cm across) and stirrer (Precision Scientific Mag-Mix, set at speed 5, the medium rate). Steam was passed through the jacket of the reaction vessel for 100° reactions. A small portion of the acid-free crude product was used for chlorine analyses, ir spectra, etc., and the remainder was chromatographed on a silicic acid column (if there was no stearic acid in the reaction product) or on a Florisil column (stearic acid present). Two typical reactions (A and B below), are described in detail. All other reactions follow the typical procedures, generally differing in only one reaction variable and the absence or presence of stearic acid. In all *cis*-9-octadecene and 1-octadecene reactions 2.00 g of the olefin has been used. The same weight was used for the 1-octadecanol reactions, (C and D below), but not for the 9-octadecanol reactions (0.20 g used for each reaction owing to restricted amounts available).

**A.—cis-9-Octadecene** (2.00 g, 0.79 mmol) was weighed into the reaction vessel and the air was displaced with nitrogen. Deuterio-perchloric acid (67.3%, 1.23 g, 0.81 mmol) was weighed drop by drop into the reaction vessel, where it passed through the octadecene to form a lower layer. A slight positive pressure of nitrogen was applied, magnetic stirring (medium rate) was begun, and steam was passed through the vessel jacket for a reaction time of 3 hr. The reaction mixture was poured into water (200 ml) and (under nitrogen) continuously benzene extracted overnight. The benzene was evaporated off to leave a crude product (2.03 g) whose ir spectrum (liquid film) showed strong absorption due to perchlorate (710, 1020, 1220, and 1250  $\text{cm}^{-1}$ ) and *trans* unsaturation (970  $\text{cm}^{-1}$ ) and weak absorption due to deuterium (2170  $\text{cm}^{-1}$ ).<sup>14</sup> Part of the crude product was analyzed for weight per cent of chlorine and the remainder (1.80 g) was chromatographed on a silicic acid (50 g) column (i.d. 2.9 cm). Elution with distilled Skellysolve B gave octadecenes (1.73 g, corrected yield 97.5%); elution with increasing concentrations (1, 10, and 50%) of diethyl ether in Skellysolve B gave an oxygenated hydrocarbon (0.004 g, corrected yield 0.2%) containing some hydroxyl and carbonyl (ir absorption at 3700 and 1700  $\text{cm}^{-1}$ , respectively). Gas chromatography indicated the latter material to be mainly polymeric (very small peak in the region of octadecanol retention time for the heavy load of material injected). The octadecene product was subjected to oxidative cleavage and mass spectrometric analysis to obtain the double-bond distribution and deuterium composition. Glpc (SE-30, 200°) showed a single peak, with retention time of *cis*-9-octadecene, and no branched chain olefin of shorter retention time.

**B.—cis-9-Octadecene** (2.00 g, 0.79 mmol) was weighed into the nitrogen-flushed reaction vessel followed by deuterio-perchloric acid (67.3%, 1.21 g, 0.80 mmol) and stearic acid (2.00 g, 0.70 mmol). The materials were allowed to react for 3 hr, at 100° under nitrogen, and with magnetic stirring. The reaction mixture was then poured into water (200 ml) and con-

(13) C. R. Eddy, J. S. Showell, and T. E. Zell, *J. Amer. Oil Chemists' Soc.*, **40**, 92 (1963).

(14) R. N. Jones and C. Sandorfsky, "Chemical Applications of Spectroscopy," *Technique of Organic Chemistry*, A. Weissberger, Ed., Vol. IX, 1961, pp 335, 407–408.

(12) (a) Reference to a particular company product does not imply endorsement of its products by the Department of Agriculture over others not mentioned. (b) See ref 4 for safety precautions to be taken with all perchloric acid reactions.

tinuously benzene extracted overnight, in an atmosphere of nitrogen. The benzene was evaporated from the extract to give a crude reaction product (4.07 g), the ir spectrum (carbon disulfide) of which showed the presence of *trans* olefin (970  $\text{cm}^{-1}$ ), carboxylic acid (1700  $\text{cm}^{-1}$ ), ester (1745  $\text{cm}^{-1}$ ), and octadecyl perchlorate ester. Part (3.68 g) of the crude product was chromatographed on a Florisil (100 g) column (i.d. 2.9 cm). Elution with Skellysolve B gave octadecene (1.36 g, corrected yield 75.2%); the ir spectrum (liquid film) showed a quite strong deuterium absorption band (2175  $\text{cm}^{-1}$ ). Further elution with Skellysolve B and 2% diethyl ether in Skellysolve B yielded octadecyl stearates (0.873 g, corrected yield 22.7% based on *cis*-9-octadecene). The consolidated ester fraction was a low melting solid but was eluted from the column first as a liquid and then as a solid. The octadecyl stearate fraction was identified as such by alkaline cleavage (see below). Continuing elution with up to 50% diethyl ether in Skellysolve B gave oxygenated hydrocarbon (0.01 g; corrected yield 0.8% based on *cis*-9-octadecene). Finally, stearic acid (1.71 g, corrected recovery 72.4%) was eluted using 1% acetic acid in diethyl ether. The stearic acid had a melting point and mixture melting point of 68.5–69.5°; mass spectrometric analysis showed the presence of only 0.004 deuterium atom/mol. The recovered octadecene was examined by oxidative cleavage and mass spectrometric analysis. Glpc (SE-30) showed the presence of a small amount of material of shorter retention time than the principal peak. Hydrazine hydrate reduction of the octadecene product to octadecane and chromatography of the octadecane showed the presence (0.6%) of shorter retention time material, presumably branched-chain  $\text{C}_{18}$  hydrocarbon.<sup>15</sup>

C.—1-Octadecanol (2.01 g 7.43 mmol) was allowed to react with aqueous deuterioperchloric acid (67.3%, 1.10 g, 7.30 mmol) for 3 hr, at 100°, under nitrogen, and with magnetic stirring. The reaction mixture was worked up in the usual way to give a crude product (2.01 g) which was chromatographed on a Florisil (50 g) column (i.d. 2.9 cm). Elution with Skellysolve B gave a very heavily deuterated hydrocarbon (0.165 g, 8%) containing some perchlorate (ir spectrum); further elution with 20% diethyl ether in Skellysolve B gave an incomplete separation of di-*n*-octadecyl ether and 1-octadecanol. The latter mixture was rechromatographed on a silicic acid (100 g) column (i.d. 2.9 cm). Di-*n*-octadecyl ether (0.800 g, 41.2%), mp 60–61°, ir absorption band at 1120  $\text{cm}^{-1}$ , was eluted by Skellysolve B followed by 5% diethyl ether in Skellysolve B. 1-Octadecanol (0.837 g, recovery of 41.6%) was eluted with diethyl ether and had mp 56.8–57.5°, mmp 56.9–57.7° with the starting 1-octadecanol. The di-*n*-octadecyl ether was recrystallized from petroleum ether to give material (0.61 g, 15.7%) with mp 60.8–61.2° (lit.<sup>16</sup> mp 62–63°). *Anal.* Calcd for  $\text{C}_{36}\text{H}_{74}\text{O}$ : C, 82.68; H, 14.26. Found: C, 82.51; H, 14.56.

The virtual absence of deuterium in the ether and recovered alcohol was shown by examination of the ir spectra (carbon tetrachloride).

D.—1-Octadecanol (2.01 g 7.43 mmol), stearic acid (2.10 g 7.38 mmol), and deuterioperchloric acid (67%, 1.11 g, 7.36 mmol) were allowed to react for 3 hr, at 100°, under nitrogen, and with magnetic stirring. The ir spectrum (carbon disulfide) indicated the reaction product to be almost solely ester. The product was chromatographed on a silicic acid (50 g) column (i.d. 2.9 cm). Elution with Skellysolve B and 5% diethyl ether in Skellysolve B gave octadecyl perchlorate (0.03 g, 1.2%), presumed to be *n*-octadecyl perchlorate, the ir spectrum of which showed very intense absorption bands (710, 1020, 1220, and 1250  $\text{cm}^{-1}$ ), characteristic of perchlorates. Continuing elution with 5% diethyl ether in Skellysolve B gave *n*-octadecyl stearate (3.76 g, 94%), mp 60–61°. Diethyl ether (30%) in Skellysolve B eluted stearic acid (0.07 g, recovery 2.9%) and diethyl ether elution gave 1-octadecanol (0.02 g, recovery 1.0%). The *n*-octadecyl stearate was recrystallized from benzene to give material (3.46 g, 88.7%) with mp 60.3–61.1° (lit.<sup>17</sup> mp 57–58°). The ir spectrum (carbon tetrachloride) showed no deuterium absorption.

*Anal.* Calcd for  $\text{C}_{36}\text{H}_{72}\text{O}_2$ : C, 80.52; H, 13.42. Found: C, 80.61; H, 13.42.

**Fusions in Molten Alkali.** A.—Octadecyl stearates (0.25 g, from the *cis*-9-octadecene–stearic acid–aqueous deuterioperchloric acid reaction, 1.0:0.9:1.0 molar ratios, 3 hr at 100°) were fused with potassium hydroxide (3.0 g) in a closed nickel pot through which a stream of nitrogen was passed. The reaction was carried out at 300°, for 1 hr, and with mechanical stirring. During the course of the reaction some distillate (0.02 g) was trapped. The pot product was dissolved in water, acidified, and extracted with ether. The ether was removed from the dried ( $\text{Na}_2\text{SO}_4$ ) extract to give a solid (0.10 g), which was methylated (boron trifluoride–methanol). Glpc (SE-30) of the methylated product gave as the principal peak methyl stearate (97.6%); also present (as % of stearate peak) were  $\text{C}_{17}$  (2.0%),  $\text{C}_{16}$  (0.4%), and traces of  $\text{C}_7$ – $\text{C}_{15}$  esters, inclusive. Examination by mass spectrometry of the methyl stearate showed, from the stearate molecular-ion peak, that no detectable amount of deuterium was present (any small amount of deuterium originally in the  $\alpha$ -methylene position of the stearic acid would be exchanged out during the fusion with alkali).<sup>18</sup> The ir spectrum (liquid film) of the oil distillate showed the presence of carbonyl (1715  $\text{cm}^{-1}$ ), deuterium (2150  $\text{cm}^{-1}$ ), and hydroxyl (3380  $\text{cm}^{-1}$ , broad band) in the oil. Glpc (SE-30) showed the principal material to have the same retention time as a sample of 9-octadecanol; a smaller peak (10%) had a shorter retention time. These results are interpreted as follows. The alkali fusion of octadecyl stearates gives initially isomeric octadecanols and stearic acid. Part of the octadecanol mixture then undergoes dehydrogenation to the corresponding ketones, and a very small fraction of the ketones undergo hydrolysis to carboxylic acids.<sup>19</sup> The 300° temperature necessary for the latter step causes the volatilization of the bulk of the octadecanols or -ones. Although no quantitative analysis was possible the results indicate the octadecyl stearates to be a mixture of all possible secondary isomers.

B.—Octadecyl stearates (0.25 g from the 1-octadecene–stearic acid–aqueous deuterioperchloric acid reaction, 1.0:1.0:1.0 molar ratios, 3 hr at 100°) were fused with potassium hydroxide (6 g, powdered) in the nickel pot under nitrogen (no flow) for  $\frac{3}{4}$  hr at 200°, and with mechanical stirring. The reaction mixture was dissolved in water, acidified, and ether extracted. The ether was removed from the dried ( $\text{Na}_2\text{SO}_4$ ) extract to yield the product (0.186 g). Chromatography of the product on a Florisil (20 g) column (i.d. 1.6 cm) gave octadecanols (0.045 g, 35%) and stearic acid (0.104 g, 79%). The low melting octadecanols had the same retention time on glpc (SE-30, 200°) as 9-octadecanol; the ir spectra of product and standard were virtually identical except that the reaction product showed a deuterium absorption band (2150  $\text{cm}^{-1}$ ). The deuterium composition of the octadecanol mixture could not be determined by mass spectrometric analysis owing to the smallness of the molecular-ion peak. However, a comparison of the intensity of the deuterium absorption bands in the ir spectra of the octadecanols from the alkali fusion of the octadecyl stearates and those of the octadecene product from the original aqueous deuterioperchloric acid reaction indicated about the same amount of deuterium in each product (similarly for the octadecanols in A above when compared with the corresponding octadecene product). Glpc (SE-30, 200°) of the methylated stearic acid fusion product showed the absence of any lower acid methyl esters (the fusion temperature being too low for the further reaction of the octadecanols); mass spectrometric analysis showed the absence of deuterium.

**Analytical Procedures.**—Oxidative cleavage of the octadecene products was carried out by the Subbaram and Youngs<sup>20</sup> modification of the von Rudloff<sup>21</sup> method. The carboxylic acids were methylated by boron trifluoride–methanol (Applied Science Laboratories) and analyzed by glpc (F & M Model 500) on an SE-30 column at 200°. The deuterium composition of octadecene and methyl stearate products was determined by C. J. Dooley using a Consolidated Electrodynamics Corp. Model 21-103c mass spectrometer; measurement of the molecular-ion and following peak intensities gave the deuterium composition after making allowances for naturally occurring deuterium. Ir spectra were

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taken on a Perkin-Elmer Infracord, Model 137. Melting points were determined using a capillary melting point apparatus. Fusions in molten alkali were carried out in a nickel pot of the same design and size as used by Weedon and coworkers.<sup>22</sup> Column chromatography involved the use of either silicic acid (Mallinckrodt, 100 mesh) or Florisil (Floridin Co.) as adsorbent.

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**Registry No.**—*cis*-9-Octadecene, 1779-13-1; deuterioperchloric acid, 19029-50-6; oleyl tosylate, 6110-54-9; 1-octadecanol, 112-92-5.

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